U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-299 459

Chlorofluoromethanes Their Thermal Stability in Passing through Cigarettes

(U.S.) Environmental Sciences Research Lab, Research Triangle Park, NC

1978

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. PB 299459
EPA-600/J-78-126	JOURNAL ARTICLE	

4. TITLE AND SUBTITLE	5. REPORT DATE
CHLOROFLUOROMETHANES: THEIR THERMAL STABILITY IN PASSING THROUGH CIGARETTES	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Philip L. Hanst, John W. Spence and Frank R. Clay	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	10. PROGRAM ELEMENT NO. 1AA603 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

REFERENCE: Am. Ind. Hyg. Assoc. J., 39: 772-776, September 1978

16. ABSTRACT

Tests have been carried out to determine whether chlorofluoromethanes in air are appreciably decomposed on pssing through lighted cigarettes. Fourier transform infrared spectroscopy was used to see if CCl_3F or $CHClF_2$ might yield $COCl_2$, COClF, or COF_2. None of these decomposition prodcts was seen, even though measurement sensitivity was high enough to reveal a conversion of one one-thousandth of the starting material. It is concluded that chlorofluoromethane pollutants in room air do not pose any greater health hazard to smokers than to non-smokers.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Halohydrocarbons * Thermal stability Infrared spectroscopy	Cigarettes	13B 07C 20M 14B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	7
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE A02-A01

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-600/J-78-126
JOURNAL ARTICLE

Chlorofluoromethanes: their thermal stability in passing through cigarettes

PHILIP L. HANST, JOHN W. SPENCE and FRANK R. CLAY
Environmental Sciences Research Laboratory, U. S. Environmental Protection Agency,
Research Triangle Park, North Carolina 27711

Tests have been carried out to determine whether chlorofluoromethanes in air are appreciably decomposed on passing through lighted cigarettes. Fourier transform infrared spectroscopy was used to see if CCl_3F or $CHClF_2$ might yield $COCl_2$, COClF, or COF_2. None of these decomposition products was seen, even though measurement sensitivity was high enough to reveal a conversion of one one-thousandth of the starting material. It is concluded that chlorofluoromethane pollutants in room air do not pose any greater health hazard to smokers than to non-smokers.

introduction

It has long been recognized that chlorofluoromethanes (CFM's) in air can be decomposed at high temperatures, yielding poisonous products.[1] The orange glow of a lighted cigarette indicates temperatures in the range of 1100 to 1200 degrees Kelvin. In this temperature range a halocarbon molecule may only last for a few seconds before it ruptures at one of its C-Cl bonds. Thus it seems possible that persons smoking cigarettes in air contaminated with CFM's could be exposing themselves to the poisonous decomposition products. Speculation about such decomposition arose earlier this year in connection with the "Legionnaires Disease" that occurred in Philadelphia in 1976.[2] At first consideration, this explanation of the Philadelphia mishap appeared plausible. A leaky air conditioning system could have fumigated smokers with large amounts of trichlorofluoromethane that might have decomposed in the cigarettes. While it is now accepted that the Legionnaries died from a bacterial infection, the question of possible dangers from cigarette smoking in the presence of CFM's still deserves an answer.

Recent research on the problem of the CFM's in the ambient air has indicated the pathways of decomposition and the identity of the reaction products.[3,4] A controlling factor is the weakness of the C-Cl bond (70 kilocalories per mole) relative to the C-F bond (120 kilocalories per mole). A C-Cl bond will break first, yielding a free radical that is attacked by oxygen. The free radicals of interest have been produced in the laboratory by the abstraction of hydrogen from the appropriate related compound, and their oxidation to stable products has been followed by the infrared absorption technique.

The thermal decomposition of carbon tetrachloride will yield CCl_3 radicals, which will then react with oxygen to yield phosgene.[4]

$$CCl_4 \xrightarrow{\Delta} CCl_3 + Cl$$

$$CCl_3 + O_2 \longrightarrow COCl_2 + ClO$$

The $COCl_2$ will be stable in the atmosphere, while the ClO will react further to yield hydrogen chloride.

The decomposition of trichlorofluoromethane similarly proceeds by way of the CCl_2F radical to yield carbonyl chloro fluoride, COClF:

$$CCl_3F \xrightarrow{\Delta} CCl_2F + Cl$$

$$CCl_2F + O_2 \longrightarrow COClF + ClO$$

If the CFM is a type that is not fully halogenated, an additional path for decomposition in air is provided through the abstraction of a hydrogen atom by an oxygenated radical such as OH. Chlorodifluoromethane, $CHClF_2$, (Fluorocarbon 22), for example, will yield carbonyl fluoride as a result of either hydrogen abstraction or thermal bond breaking.

$$CClF_2 + O_2 \longrightarrow COF_2 + ClO$$

experimental method

The question to be answered is not whether chlorofluoromethanes can be decomposed thermally, but to what extent the compounds

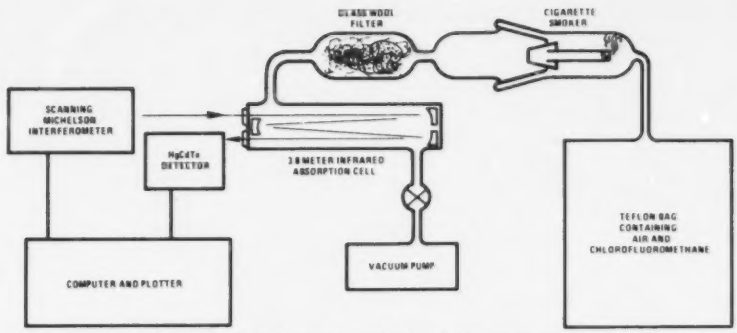

Figure 1 – System for analysis of cigarette smoke

can be decomposed in passing through a cigarette. What matters is whether the compound is exposed to a high enough temperature for a long enough time for the degree of decomposition to be appreciable. A rough estimate of the rate of thermal decomposition can be made from the unimolecular rate expression:

$$k = A \cdot \exp(-\Delta E\ RT)$$

Using a value of $A = 10^{13}$ sec^{-1}, as quoted for the rupture of the 70 KCal C-Cl bond in dichloroethane,[5] yields half-lives of 0.35 seconds at 1100 °K and 5.5 seconds at 1200 °K. Since the temperature, the rate of air flow, and the true value of A are all uncertain, a firm prediction of decomposition cannot be made. Experimental measurements are required. In the present experiments chlorofluoromethane-air mixtures were passed through lighted cigarettes at a typical smoking rate.

Infrared absorption was chosen for analysis because it yields unequivocal quantitative detection of the chlorofluoromethanes and their decomposition products. The phosgene, carbonyl chloro fluoride and carbonyl fluoride molecules all show strong characteristic infrared bands in spectral regions where there is no interferehee from the parent compounds or from the many tobacco decomposition products in cigarette smoke.[6] The experimental system consisted of the following components: (1) an infrared spectrometer, (2) an infrared absorption cell, (3) a cigarette smoking apparatus, and (4) a source of the air-chlorofluorocarbon mixture. This system was assembled in the laboratory, as diagrammed in Figure 1.

The infrared cell was a small multiple pass cell of novel design in which a 3.8 meter path was folded within a tube 50 centimeters long with a 200 cc volume. The cigarette smoking apparatus included a standard taper ground glass joint with glass connecting tubes. Inserted within the inner member of the glass joint was a cork stopper with a tapered hole to hold the cigarette. The joint was opened for placement and removal of the cigarette. The cylindrical volume surrounding the cigarette was about 2.5 cm. in diameter and 15 cm. long. Unfiltered Camel cigarettes were used. Particulate matter was trapped on a glass wool filter 2.5 cm. in diameter and 30 cm. long, located between the cigarette smoking device and the infrared absorption cell. It was demonstrated in a test that 5 ppm of phosgene in air passed through this filter without loss. The chlorofluoromethanes were taken from lecture bottles and mixed with room air in a Teflon bag of approximately 50 liters volume. A small amount of suction from a vacuum line drew the polluted air from the bag through the cigarette and on into the infrared cell. The infrared spectrum was recorded on a Fourier Transform Spectrometer at a resolution of 2 wave numbers.

The experiments were carried out as follows:

(1) The polluted air mixture was slowly drawn through the infrared cell with no cigarette in place, and the spectrum was recorded. This spectrum allowed calculation of the percentage of chlorofluoromethane pollutant in the air.

(2) A lighted cigarette was placed in its holder in the air stream. After about 30

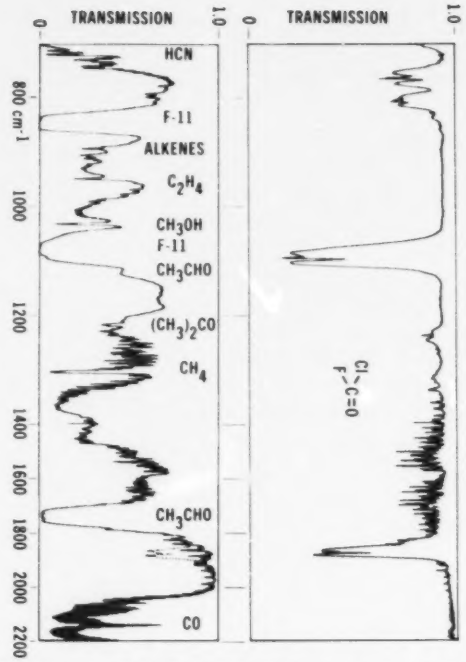

Figure 2 – **(Top)** Spectrum of approximately 1 ppm carbonyl chloro fluoride formed in the oxidation of dichlorofluoromethane. Path, 360 meters. **(Bottom)** Spectrum of gaseous components of smoke when the air contained 2000 ppm CCl_3F. Path, 3.8 meters.

seconds, during which the cigarette burned down about 3 cm. the air flow was stopped and the infrared spectrum was recorded.

(3) The spectra were plotted in ratio mode against the spectrum of the empty cell as well as against each other. The amounts of reactants and products were calculated with the aid of reference spectra available in the literature.

results

Two pollutants were tested: Trichlorofluoromethane (CCl_3F), at 2000 parts-per-million (ppm) and chlorodifluoromethane ($CHClF_2$) at 2500 ppm. The usual variety of toxic combustion products from the tobacco was evident in the infrared spectrum along with the unreacted chlorofluoromethane. However, neither of the chlorofluoromethane compounds yielded any detectable amount of the carbonyl compound that would result from its decomposition.

Since the absorption bands of the carbonyl compounds being sought are strong bands and are not overlapped by the spectra of any of the other reaction products, a low upper limit can be placed on the amounts of the carbonyl chloro fluoride and carbonyl fluoride that could have been present in the products. This upper limit is approximately 2 ppm. In contrast, the amounts of some other poisonous gases detected in the smoke were as follows: hydrogen cyanide, 200 ppm; methanol, 400 ppm; acetone, 40 ppm; acetaldehyde, 1300 ppm; nitric oxide, 240 ppm; and carbon monoxide, 8000 ppm.

Figure 2, lower part, shows a spectrum of the gaseous portion of the smoke in the case where trichlorofluoromethane (CCl_3F) was tested. The compounds responsible for the principal absorption bands are identified. No bands of phosgene or of carbonyl chloro fluoride are evident. For comparison, the upper portion of Figure 2 shows the spectrum of approximately one ppm of carbonyl chloro fluoride produced by the oxidation of one ppm fluorocarbon 21 ($CHCl_2F$), using the chlorine atom method of initiating the oxidation. The infrared path length for the upper spectrum was 360 meters. It is to be noted that the upper spectrum shows no trace of phosgene. Based on the upper spectrum a dotted line has been drawn on the lower spectrum to show how the region near 1880 cm^{-1} would have appeared if one percent of the trichlorofluoromethane had decomposed thermally, yielding 20 ppm of carbonyl chlorofluoride. It is obvious that any actual yield of the product must have been much smaller than 20 ppm. A maximum of 2 ppm seems to be a fair estimate.

To be doubly sure of these results the test was also run with no glass wool filter in the line. Although the particulate matter fouled the infrared cell badly, it could still be seen after the particles settled that the gaseous products were the same as those seen with the filter, and that there was no evidence of carbonyl chloro fluoride.

Figure 3 shows a spectrum of the gaseous portion of the smoke in the case where chlorodifluoromethane, $CHClF_2$ (fluorocarbon 22) was tested. The upper part of the figure shows the spectrum that resulted when the cigarette was smoked in uncontaminated room

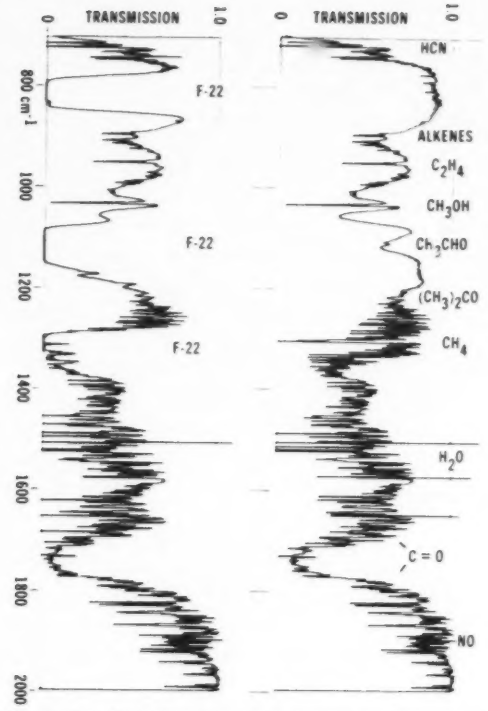

Figure 3 – **(Top)** Spectrum of gaseous components of smoke when the air was uncontaminated. Path 3.8 meters. **(Bottom)** Spectrum of gaseous components of smoke when the air contained 2500 ppm $CHClF_2$. Path, 3.8 meters.

air. The compounds responsible for the principal absorption bands are identified. The lower part of the figure shows the spectrum obtained when the room air was polluted with 2500 ppm of $CHClF_2$. The products of the burning tobacco show amounts of infrared absorption almost identical with those in the upper spectrum but with the strong bands of the chlorodifluoromethane superimposed. There are no bands that can be attributed to products of decomposition of the chlorodifluoromethane.

Figure 4, top, shows the spectrum of the chlorodifluoromethane-air mixture that was passed through the cigarette in the experiment that produced Figure 3. This is simply the spectrum obtained while the polluted air was flowing through the apparatus before the cigarette was lighted. The bottom spectrum of Figure 4 is a ratio plot of the lower spectrum of Figure 3 divided by the upper spectrum of Figure 3. In this ratio plot the absorption bands of the tobacco products are nearly fully cancelled, showing that the tobacco combustion was nearly the same whether or not the chlorodifluoromethane was present. The main absorption bands in the ratio plot are due to the chlorodifluoromethane that passed through the cigarette. These bands are almost identical with those in the upper spectrum, demonstrating clearly that there was no loss of chlorodifluoromethane as it passed through the lighted cigarette. Furthermore – and even more important – the ratio plot does not show any absorption due to carbonyl fluoride. If the latter compound had been formed in as much as one percent yield (25 ppm), its absorption bands would appear in the ratio plot as indicated by the dotted lines. Thus the spectra make it clear in two ways that chlorodifluoromethane was not decomposed: (1) all the chlorodifluoromethane

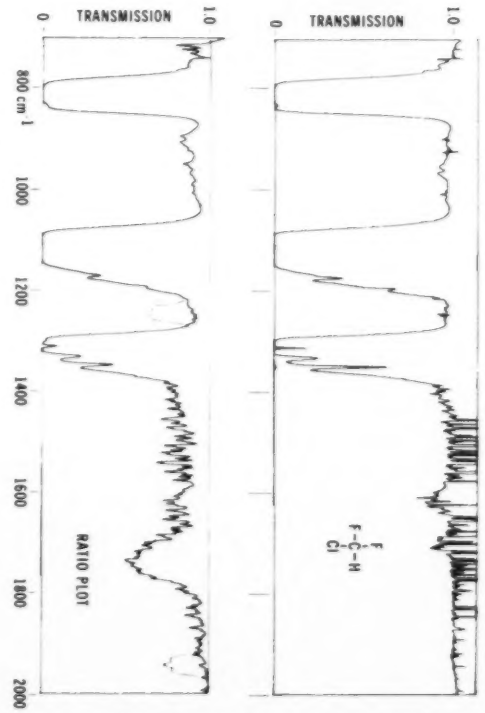

Figure 4 – **(Top)** Spectrum of air containing 2500 ppm $CHClF_2$. Path, 3.8 meters. **(Bottom)** Ratio plot from spectra of Figure 2, lower divided by upper. Dotted lines show where bands of COF_2 would appear if they were present.

that entered the burning cigarette passed through and was seen beyond; and (2) there was no evidence of carbonyl fluoride.

conclusion

An experiment has been carried out under simulated smoking conditions that might occur in a room polluted by trichlorofluoromethane (F-11) or by chlorodifluoromethane (F-22). Infrared analysis of the cigarette smoke showed that the reaction products carbonyl chloro fluoride and carbonyl fluoride were not formed in yields higher than 0.1 percent. As far as the instruments could show, all the chlorofluoromethane passed through the lighted cigarette without decomposition. It seems reasonable to conclude that chlorofluoromethane pollutants in room air do not pose any greater health hazard to smokers than to non-smokers.

references

1. **Midgely, T., Jr. and A. L. Henne:** Decomposition of Dichlorodifluoromethane by Flames. *Ind. Eng. Chem. 24*:641 (1932).
2. **Altman, L. K.:** Environmental Group Contends Fluorocarbon Refrigerant Poses Wide Threat. New York Times, pg. B-22 (December 15, 1976).
3. **Spence, J. W., P. L. Hanst and B. W. Gay, Jr.:** Atmospheric Oxidation of Methyl Chloride, Methylene Chloride, and Chloroform. *J. Air Pollut. Control Assoc. 26*:994 (1976).
4. **Rowland, F. S. and M. J. Molina:** Chlorofluoromethanes in the Environment. Atomic Energy Commission Report No. 1974-1, University of California, Irvine. (1974).
5. **Benson, S. W.:** The Foundations of Chemical Kinetics. p. 262. McGraw-Hill N.Y. (1960).
6. **Neilson, A. H., T. G. Burke, P. J. H. Woltz and E. A. Jones:** The Infrared and Raman Spectra of F_2CO, FClCO and Cl_2CO. *J. Chem. Phys. 20*:596 (1952).